Pestic. Sci. 1998, **54**, 418–434

Assessing the Ground-Water Contamination Potential of Agricultural Chemicals: a Flexible Approach to Mobility and Degradation Studies†

Margaret S. Mills[1]* and Nick D. Simmons[2]

[1] Zeneca Agrochemicals, Jealott's Hill Research Station, Bracknell, Berkshire RG42 6ET, UK
[2] Zeneca Agricultural Products, 1800 Concord Pike, Wilmington, DE, 19850, USA

(Received 6 July 1998; revised version received 21 August 1998; accepted 28 August 1998)

Abstract: Understanding the fate of agrochemicals in surface and sub-surface environments is of vital importance for the protection of water quality and for responsible environmental stewardship of crop-protection products. This paper demonstrates the need for a versatile approach to study experimental designs, aimed at a fuller understanding of the mobility and degradation of particular compounds in surface and sub-surface environments. Where appropriate, the environmental profile of a crop-protection product is built up using a combination of the following four study types: (a) radiolabelled laboratory studies to establish the routes of degradation and key degradates, supported by non-radiolabelled small-scale field studies to quantify key degradates under field conditions; (b) small-plot radiolabelled field studies for tracking the fate of products with low usage rates or those exhibiting rapid and extensive metabolism; (c) small-scale prospective ground-water studies (PGWs) to assess the potential for a compound's sub-surface mobility in vulnerable ground-water settings, and (d) large-scale ground-water monitoring studies to measure actual environmental concentrations of an in-use product. The determination of which studies are required is product-specific. Examples include radiolabelled laboratory and field studies conducted to investigate the rapid dissipation of the post-emergence herbicide tralkoxydim and its subsequent metabolites in surface soil. A PGW approach is illustrated, used to assess the degradation and mobility of the contact herbicide fomesafen under vulnerable ground-water conditions. Finally, large-scale monitoring studies are described which are used to assess the impact of the selective post-emergence herbicide fluazifop-P-butyl and fomesafen in vulnerable ground-water regions of northern Italy and Germany. These examples illustrate how flexibility and diversity of study design are essential to the development of a meaningful database of environmental fate information for crop-protection products. Such a database provides critical data for risk assessments and predictive modelling, and enhances our fundamental understanding of environmental science. © 1998 Society of Chemical Industry

Pestic. Sci., **54**, 418–434 (1998)

Key words: groundwater contamination; tralkoxydim; fomesafen; fluazifop-butyl; modelling

* To whom correspondence should be addressed.
† One of a collection of papers on various aspects of agrochemicals research contributed by staff and collaborators of Zeneca Agrochemicals UK and Zeneca Ag Products USA. The papers were collected and collated by Dr B. C. Baldwin and Dr D. Tapolczay.

 Pestic. Sci. 0031–613X/98/$17.50. Printed in Great Britain

1 INTRODUCTION

Crop-protection products are in an integral part of agriculture world-wide and ensure the efficient production of quality food at low cost. However, heightened public concern over water quality,[1–3] and the corresponding increase in the regulatory requirements for the registration of agrochemicals, demands both an early and thorough appraisal of the environmental fate of products.

The fate of a pesticide from its point of application, through surface soil and into subsoil, is governed by the interactive processes of adsorption, transformation and transport.[4] Understanding the science behind such dissipation routes is key to ensuring the accurate assessment of environmental behaviour and vital in securing the sustained registration of new and existing products.[5] Additionally, it is fundamental to developing and validating computer simulation models for use as predictive tools in future environmental fate assessments.[6]

Quantifying the mobility and degradation of pesticides in surface soil and sub-soil under field conditions presents a challenge. Attempts to recreate 'field conditions' in the laboratory can lead to artefacts and the erroneous quantification of dissipation behaviour, and the validity of such studies is sometimes questioned.[7] Additionally, the micro- and macro-variability of the agricultural field environment adds to the complexity of quantifying the dissipation process.[8] In order to overcome these practical difficulties a flexible and diversified approach to study design is essential.

The objective of this paper is to illustrate a number of alternative laboratory and field study designs to aid the development of a meaningful environmental fate database for crop-protection products. In particular, it focuses on investigating the mobility and degradation of products in surface soil and sub-soil environments. Environmental fate profiles are built up by a combination of radiolabelled and non-radiolabelled laboratory and field studies of varying complexity. Radiolabelled laboratory studies often provide core data on the route of degradation of crop-protection products in soil. Subsequent unlabelled field studies, using formulated material, determine the dissipation of the parent compound and the importance of key metabolites. Alternatively or additionally, small-scale radiolabelled field studies may be employed for products with extremely low use rates, or those exhibiting rapid and extensive metabolism. The fate of the post-emergence herbicide tralkoxydim (2-[1-(ethoxyimino)propyl]-3-hydroxy-5-mesitylcyclohex-2-enone) was studied using this approach. Tralkoxydim has a short half-life in soil under laboratory conditions (DT_{50} 2–5 days), with similarly rapid degradation of the numerous primary metabolites.[9] This dissipation profile presents both detection and quantification challenges in field trials using conventional analytical techniques. For this reason, a small-scale radiolabelled field study was conducted to quantify dissipation behaviour of tralkoxydim, the results of which were confirmed by comparison with results from conventional unlabelled field trials and laboratory studies.

Whilst small-scale studies provide information on degradation rates and routes, the mobility and leaching potential for a compound is often assessed on a larger field scale to account for the wide variability of soil properties. Prospective ground-water studies (PGWs) are used to investigate both the degradation potential *and* mobility of products under a number of different field settings. Conservative tracers may also be applied to monitor water fluxes, determine when recharge of the aquifer has occurred, and to investigate the contribution of macropores to preferential flow. This PGW approach was used to monitor the potential for residues of the post-emergence herbicide fomesafen (5-(2-chloro-α,α,α-trifluoro-*p*-tolyloxy)-*N*-methylsulfonyl-2-nitrobenzamide) to move to shallow ground-water. This study was conducted under 'worst case' conditions, on a sandy soil or low organic matter, shallow water table, and with irrigation applied to supplement rainfall to ensure total precipitation far in excess of average annual rainfall.

The data generated in these diverse studies can provide important refinements to simulation models and provide confident estimates of leaching potential and possible ground-water contamination. Modelling of the leaching process is well advanced, and in particular PRZM (pesticide root-zone model), developed by the US-EPA is widely used to estimated soil-pore water and ground-water residue concentrations.[10] The calibration and validation of PRZM for predicting the dissipation behaviour of fomesafen is described, and compared to PGW-generated field dissipation data on fomesafen. This example illustrates the useful extension of the PGW data through PRZM modelling to provide insight into potential fomesafen ground-water concentrations following many years of repeated applications.

Finally, although the impact of crop-protection products on ground-water quality can be assessed through a variety of studies and the likely concentrations estimated by simulation modelling, it is only through monitoring studies that these predictions can be confirmed, the scale of contamination assessed and the dissipation of residues followed. Such monitoring can be targeted to vulnerable areas, with shallow ground-water and high product use. This approach was used to assess the impact of the selective post-emergence herbicide fluazifop-butyl and its resolved analogue fluazifop-P-butyl [(*R*)-2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propionic acid], in high-use and vulnerable ground-water areas of Germany and northern Italy, and the pre-emergence herbicide fomesafen in northern Italy. Due to the rapid dissipation of fluazifop-butyl and fluazifop-P-butyl, residues of the major acid metabolite,

fluazifop, were monitored in wells situated in areas where the products had been applied commercially for the past five years (fluazifop-P-butyl replaced fluazifop-butyl as the active ingredient in 1989).

2 SURFACE SOIL DISSIPATION: [^{14}C]TRALKOXYDIM FIELD DISSIPATION STUDY

2.1 Materials and methods

2.1.1 Radiochemical preparation

[*Phenyl*-^{14}C]tralkoxydim was supplied by Zeneca Agrochemicals, Jealott's Hill, UK. Radiochemical purity was determined by TLC. The radiolabelled material was isotopically diluted with unlabelled tralkoxydim and the specific activity determined by HPLC and liquid scintillation counting (LSC). [^{14}C-]Tralkoxydim was then formulated as a 250 g kg^{-1} wettable powder formulation, similar in particle size to the basic particles of the commercial 5G formulation.

2.1.2 Field plot layout and preparation

The study was conducted at three trial sites in the USA in 1987 and 1988: Big Sandy, Montana (sandy loam); Champaign, Illinois (silty clay loam); and Pullman, Washington (silty clay loam). Each trial site comprised a 1-m^2 bare soil plot, divided into a sampling grid of 10-cm squares and an application grid of 1·25-cm squares, using overlying wire mesh. The plots were located in a bunded area providing protection against wind and rain erosion. Suction cup lysimeters were inserted under opposite ends of the plot *via* small pits and tunnels dug adjacent to the side of the plot at approximately 30 cm and 53 cm under the treated area at 63° and 66° angles respectively to collect leachate water. Prior to application, five control cores were taken immediately outside the treatment area for soil characterisation.

2.1.3 Radiochemical application

At each site, 100 µl of [*phenyl*-^{14}C]tralkoxydim resuspended in water to 49·8 µg ml^{-1}, 131 kBq ml^{-1}, were pipetted evenly across each 1·25 cm. This gave an application rate equivalent to approximately 350 g ha^{-1}. Samples of the application solution were taken before, during and after application to determine the exact amount applied. The application grid was removed following application.

2.1.4 Conditions of study

In Pullman, Washington, air temperatures were slightly higher than the normal 30-year average for the local area (1951–1980 weather data from Washington NOAA Station No. 45-6789), and precipitation totals were 53% and 83% of the expected normal amounts in 1987 and 1988, respectively. In Champaign, Illinois, precipitation levels in 1988 were 40% lower than the 30-year average (1951–1980 weather data from Seymour, Illinois NOAA State Station No. 39-7667). In Big Sandy, Montana, 1987 and 1988 were exceptionally dry years, with precipitation levels 58% (1987) and 81% (1988) of the 30-year average (1951–1980 weather data from Fort Assinniboine NOAA Station No. 24–3110).

2.1.5 Soil sampling

Soil samples were collected from pre-determined sampling positions on the 10-cm square sampling grid from a depth of 0–9 and 9–39 cm using zero-contamination soil corers. Depending on location, sampling intervals were 0, 1, 3, 6–8, 14–15, 27–35, 81–85 and 365–390 days after treatment (DAT). The metal corer had an interior clear butyrate liner, capped at the top, which held the core and could be removed while an exterior metal sleeve remained in the soil profile. For each sampling position, two zero-contamination cores were taken, one with an internal diameter of 4 cm for 0- to 9-cm cores, and the other a 2·3-cm internal diameter for 9- to 39-cm cores. The wider shallow metal sleeve remained in place and the narrower, deeper corer was inserted through the sleeve to prevent the ingress of contaminated surface soil. The core ends were capped before labelling, double bagging and storage on dry ice prior to shipment and subsequent analysis. At zero time 10 cores were taken at each depth. At subsequent sampling intervals only five cores were removed.

2.1.6 Soil extraction

Cores (0–9 cm) were split in half for extraction but the extracts were combined. The 9- to 39-cm cores had the top and bottom 1·25 cm discarded to eliminate possible contamination and were then divided into three discrete horizons whilst frozen. Soils were extracted by shaking for 45 min at room temperature with hexane + acetone (25 + 75 by volume; 200 ml) followed by Buchner filtration, and then re-extracted with acetone (200 ml). Extracts were brought up to volume and radioactivity measured by LSC. For zero time and one day after treatment (DAT), five cores were analysed. In 3 DAT samples, four cores were analysed. From 6 DAT onwards, soil cores were bulked and homogenised at 5°C before analysis, one mean soil core weight being taken for extraction. Soil extracts containing >2% of the applied radioactivity were reduced in volume *in vacuo* and analysed by LSC and TLC. Unextracted radioactivity was analysed by combustion of soil debris. One soil sample from each site showing a high level of unextracted radioactivity was further extracted by wrist-action shaking with sodium hydroxide solution (1 M) for 18 h. The resulting solutions were acidified and partitioned into diethyl ether (partition efficiency = 66–77%) and the ether fractions analysed by TLC.

2.1.7 Instrumentation

Liquid scintillation counting (LSC) was carried out using a 1219 Rackbeta 111 instrument (LKB Instruments Ltd, Leicester, UK). All samples were counted in duplicate and a third was checked for quench curve compatibility by fortification with a known amount of [^{14}C]toluene. Samples were counted for 10 min or for the accumulation of 10^4 counts, whichever was the sooner. Optiphase Safe (LKB Ltd) was used as the scintillant for all counting. The limit of detection was set at 0·5 Bq above background (typically 0·8 Bq). Combustion was carried out using a Harvey Biological Oxidiser (R. Harvey Instruments Co., New Jersey, USA) interfaced with a Zymark laboratory robot (Zymark Ltd, Warrington, Cheshire, UK). [^{14}C]Carbon dioxide evolved during the combustion process was trapped in a cocktail of Optiphase Safe + 2-methoxyethylamine + water (1500 + 500 + 40 by volume) and quantified by LSC. TLC plates (Camlab SIL-G25/UV254) were developed in the following solvent systems: (a) ethyl acetate + acetone + hexane (15 + 15 + 70 by volume); (b) chloroform + acetone + hexane (25 + 5 + 70 by volume); (c) dichloromethane + hexane + acetonitrile + glacial acetic acid (60 + 25 + 15 + 1 by volume); (d) hexane + acetone + chloroform + glacial acetic acid (70 + 20 + 10 + 1, by volume). TLC plates were quantified by radiochromatogram scanning using the RITA 6800 Linear Analyser (Raytest, Sheffield, UK). All chromatograms were also examined by autoradiography, using X-ray film (Hyperfilm, Betamax, Amersham International Limited, Amersham, Bucks, UK). HPLC was carried out using the following system: Pump: SP8700 (Spectra Physics, St Albans, Herts., UK); Injector: U6K (Waters Associates); Detector: LC-871 (Spectra Physics); Column: Spherisorb 5 CN (Hichrom, Reading, UK), 250 × 9 mm semi-prep. The mobile phase was hexane + dichloromethane + formic acid (75 + 25 + 1, by volume) at a flow rate of 3·5 ml min^{-1} with UV detection at 260 nm.

2.2 Results and discussion

Previous laboratory degradation studies using [^{14}C]tralkoxydim established a short half-life in a range of surface soils (2–5 days) (Simmons, N.D., Mason, R. and Bewick, D. W. ICI Agrochemicals Report, unpublished, 1987). Metabolism was extensive with numerous degradates being formed and further transformed, with the ultimate production of significant quantities of [^{14}C]carbon dioxide (Fig. 1). Furthermore, soil-surface photolysis, aqueous photolysis and hydrolysis all contribute as possible additional mechanisms of dissipation (Clarke, N. and Cavell, B. D. ICI Agrochemicals Report, unpublished, 1986; Evans, J. D. H. L. and Hadfield, S. T. ICI Agrochemicals Report, unpublished, 1988; Mason, R., Simmons, N. D. and Bewick, D. W. ICI Agrochemicals Report, unpublished, 1988). The complex metabolic profile of tralkoxydim dictated that ^{14}C-labelled field dissipation studies should be used to monitor metabolite residues under field conditions.

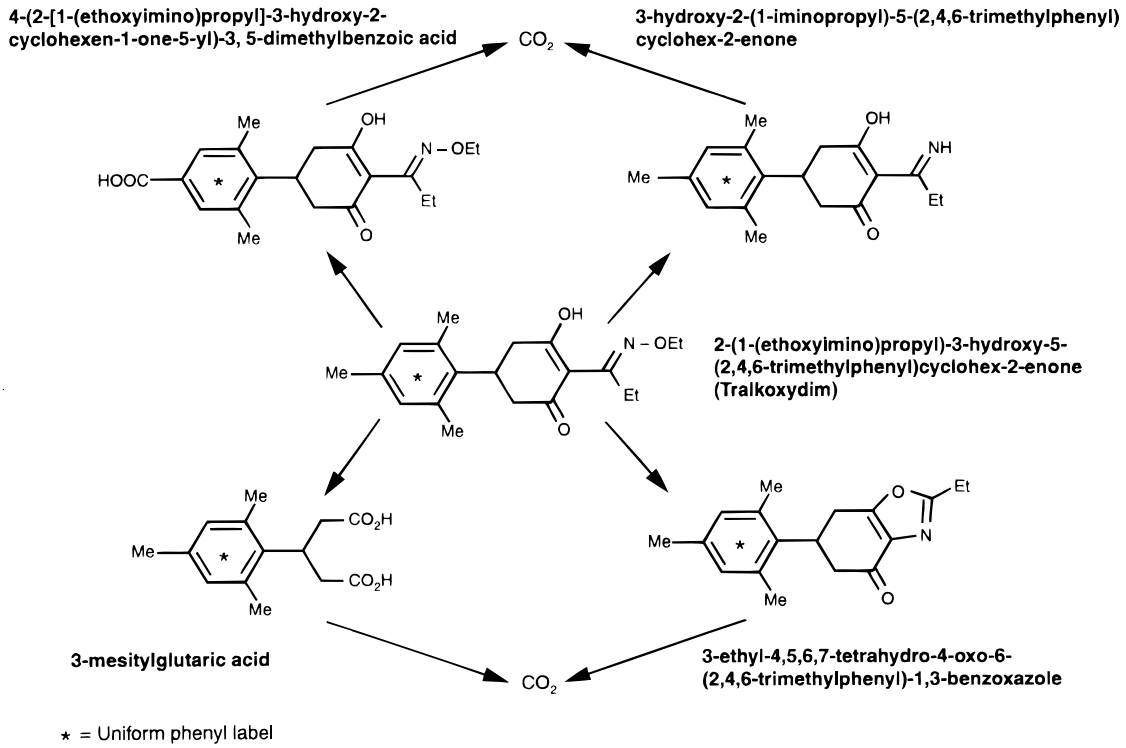


Fig. 1. Molecular structures of tralkoxydim and four major metabolites, and proposed metabolic pathway in soil.

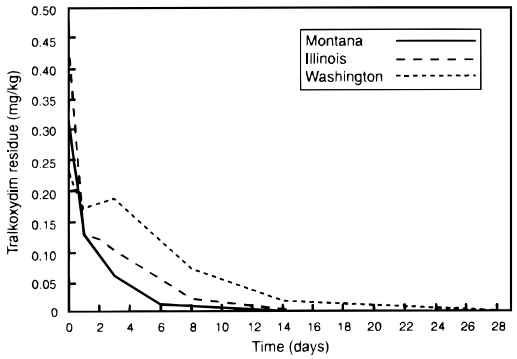


Fig. 2. Decline of tralkoxydim (mean of five or fewer cores) in silt loam (Montana) and two silty clay loams (Illinois and Washington).

At all three field sites, [^{14}C]tralkoxydim dissipated rapidly, with a half-life of <7 days (Fig. 2). These results were entirely consistent with previous laboratory studies of microbial, chemical and photolytic breakdown of tralkoxydim (Simmons, N. D., Mason, R. and Bewick, D. W. ICI Agrochemicals Report, unpublished, 1987; Clarke, N. and Cavell, B. D. ICI Agrochemicals Report, unpublished, 1986; Evans, J. D. H. L. and Hadfield, S. T. ICI Agrochemicals Report, unpublished, 1988; Mason, R., Simmons, N. D. and Bewick, D. W. ICI Agrochemicals Report, unpublished, 1988). Degradation occurred most rapidly in the sandy loam (Montana) soil where levels of [^{14}C]tralkoxydim declined to $<5\%$ of the applied radiocarbon, after one day. In the silty clay loam soils (Illinois) and (Washington), levels of [^{14}C]tralkoxydim had fallen to $<5\%$ by 8 and 35 days after treatment (DAT), respectively. These findings were in good agreement with parallel unlabelled dissipation trials carried out at the same trial sites during 1987–1988, where half-life values were found to be 1, 2 and 3·9 DAT in Montana, Illinois and Washington sites respectively (Hoag, R. E. and Riggle, B. D. ICI Americas Report, unpublished, 1989; Hoag, R. E. and Riggle, B. D. ICI Americas Report, unpublished, 1989; Hoag, R.E. and Riggle, B. D. ICI Americas Report, unpublished, 1989).

The analysis of 'zero time' cores showed levels of [^{14}C]tralkoxydim to be much lower than that applied; 42·9, 52·0 and 55·8 (mean % of applied) in Montana, Illinois and Washington soil cores, respectively. Analysis of formulated [^{14}C]tralkoxydim was carried out in the field, immediately prior to application at all sites. These results indicated that the application solutions were always $>87\%$ pure with respect to [^{14}C]tralkoxydim. The low recoveries at zero time reflect the intrinsic instability of tralkoxydim under conditions of microbial, chemical and photolytic degradation during the unavoidable time delay between application and sampling. This instability had also been documented as part of standard laboratory studies under controlled conditions (Simmons, N. D., Mason, R. and Bewick, D. W. ICI Agrochemicals Report, unpublished, 1987).

Analysis of the soil cores from 0–9 cm revealed a complex mixture of extractable residues (levels of radioactivity, both extractable and unextracted found in the 9- to 39-cm horizons were generally less than the limit of detection). The major degradation products were

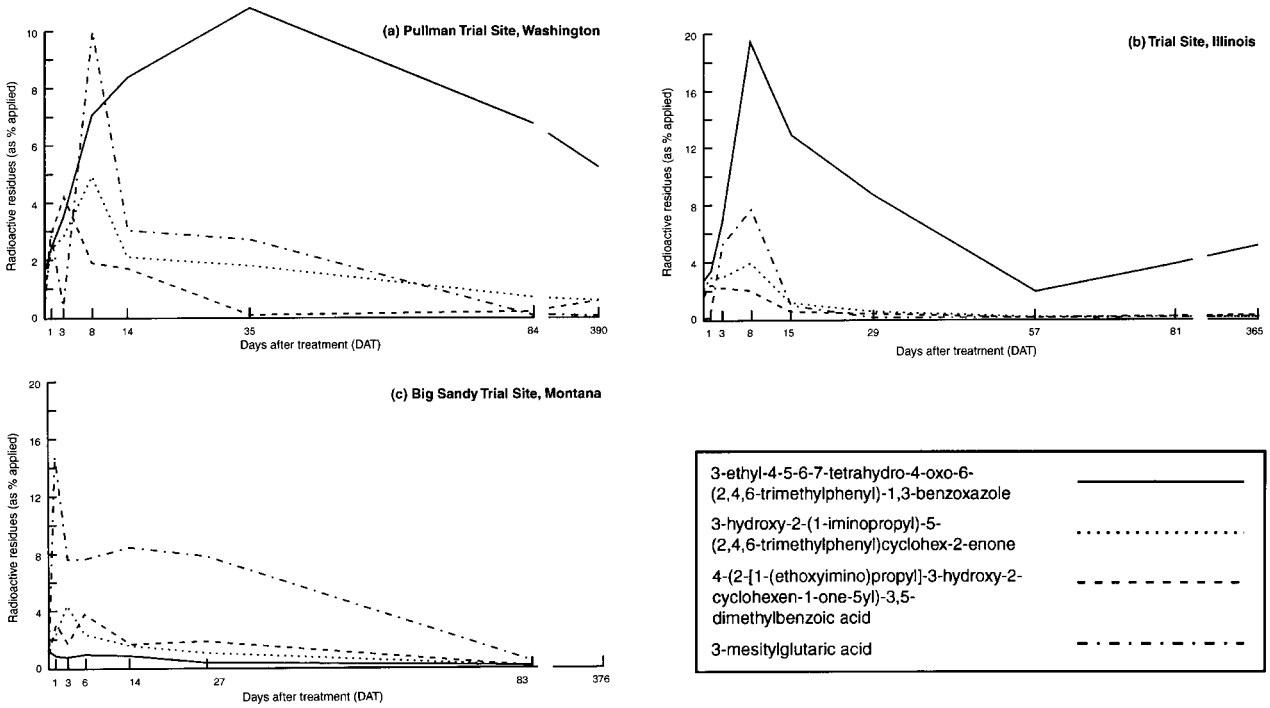


Fig. 3. Production and subsequent dissipation of tralkoxydim metabolites through time at Montana, Illinois and Washington ^{14}C field dissipation studies.

similar to those found in the previous laboratory soil metabolism study (Simmons, N. D., Mason, R. and Bewick, D. W. ICI Agrochemicals Report, unpublished, 1987). Figure 3 shows detected metabolite production and subsequent dissipation. At all three trial sites, no single component was present at levels >6% of applied radioactivity by the final sampling dates, which were 376, 365 and 390 days after treatment in Montana, Illinois and Washington trial sites, respectively.

Levels of unextractable radioactivity reached maxima after 3 days (Montana soil: 66·4%), 3 days (Illinois soil: 33·0%) and 35 days (Washington soil: 49·8% of applied radioactivity). Thereafter the levels of unextracted radioactivity decreased to 21·8%, 17·5% and 28·2% of applied radioactivity in soil after 376 (Montana), 365 (Illinois) and 390 days (Washington), respectively. Again, this decline was in good agreement with laboratory soil studies which showed up to 56·2% of the applied radioactivity was mineralised as [^{14}C]carbon dioxide throughout a 180-day incubation period (Simmons, N. D., Mason, R. and Bewick, D. W. ICI Agrochemicals Report, unpublished, 1987). In the case of the sodium hydroxide extracts, significant extractability was achieved from one soil sample in all three sites. TLC analysis showed the extract to contain traces of two metabolites (3-mesitylglutaric acid and 4-(2-[1-(ethoxyimino)propyl]-3-hydroxy-2-cyclohexen-1-one-5-yl)-3,5-dimethylbenzoic acid). The majority of radioactivity was present in baseline or strongly polar moieties. No significant levels of parent or other known metabolites were present.

Finally, soil was sampled to a depth of 39 cm and soil solution collected from 30- and 50-cm depths during the study to monitor for downward leaching. From these analyses it was concluded that no significant movement of [^{14}C]tralkoxydim or its degradation products occurred through the soil profile (<0·2% of radioactivity applied to one soil core in >300 ml collected).

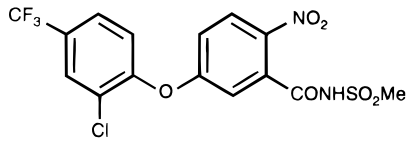
In summary, this ^{14}C-labelled field dissipation study confirmed the timing and routes of degradation of tralkoxydim already established through laboratory experiments. The study also showed the rapid dissipation of tralkoxydim metabolites under field conditions. The results supported the conclusion that tralkoxydim is rapidly and completely degraded under field conditions.

3 FOMESAFEN PROSPECTIVE GROUNDWATER (PGW) STUDY

3.1 Materials and methods

3.1.1 Study site details

A prospective ground water study (PGW) was conducted to monitor for residues of fomesafen (Fig. 4) in the unsaturated (vadose) zone and saturated zone (ground-water). The test site was located near Goldsboro, North Carolina, USA and comprised a square test plot (1 ha) situated on a fine-grained loamy sand (Kenansville loamy sand; 1% organic matter; 0·4% slope) overlying sands, loamy sands and sandy loams within the Kenansville Soil Series.[11] The surface texture extended for 30–60 cm. Despite minor discontinuous bands of sandy clay loam, there were no restrictive subsoil layers to prevent recharge. Depth to ground water was 5·2–6.1 m below ground surface (bgs).



Fomesafen

Fig. 4. Molecular structure of fomesafen (5-[2-chloro-4-(trifluoromethyl)phenoxy]-*N*-methylsulfonyl-2-nitrobenzamide).

A series of 'relatively undisturbed' 7·5-cm diameter soil cores were sampled from four positions located adjacent to the test plot for vertical hydraulic conductivity measurements. The samples were taken in 60-cm increments using steel Shelby Tubes and a mechanical auger, to a maximum depth of approximately 6 m. Core ends were sealed with paraffin wax prior to transportation at ambient temperature for laboratory vertical hydraulic conductivity determinations. Similar soil samples were shipped to A&L Laboratories (Fort Wayne, Indiana) for soil characterisation (organic matter, particle size distribution and texture, pH, cation exchange capacity, water holding capacity [at field capacity (1/3 bar) and wilting point (15 bar)] and P, K^+, Mg^{2+} and Ca^{2+} content).

3.1.2 Installation of soil water and ground-water monitoring equipment

PVC piezometers were installed at each corner of the test plot to determine water-table depth and direction of ground-water flow. An illustration of the layout of the study plot is shown in Fig. 5. Three suction-cup lysimeter clusters (I-III) (Soil Moisture Inc., Santa Barbara, CA) were installed on the test plot, each cluster comprising three separate lysimeters located at approximately 1-, 2- and 3-m depths. Additionally, three clusters of stainless steel monitoring wells were installed (MW-1 through to MW-3), each cluster comprising a shallow (screen at 2·7–4·3 m) medium (screen 5·5–7·0 m) and deep (screen 8·2–9·8 m) well to facilitate sampling of the surface of the aquifer and accommodate annual fluctuations in water-table levels (Fig. 6). Monitoring wells were sampled using permanently installed 4·5-cm diameter submersible pumps (XP100-60, KV Associates, Falmouth, MA, USA) powered by a 12-volt battery (flow rate up to 4 litre min^{-1}). Water was sampled 30 cm from the base of the medium and deep wells (the shallow wells remained dry during the study period) using PTFE tubing (1 cm ID) which was attached to a coupling valve in the well cap.

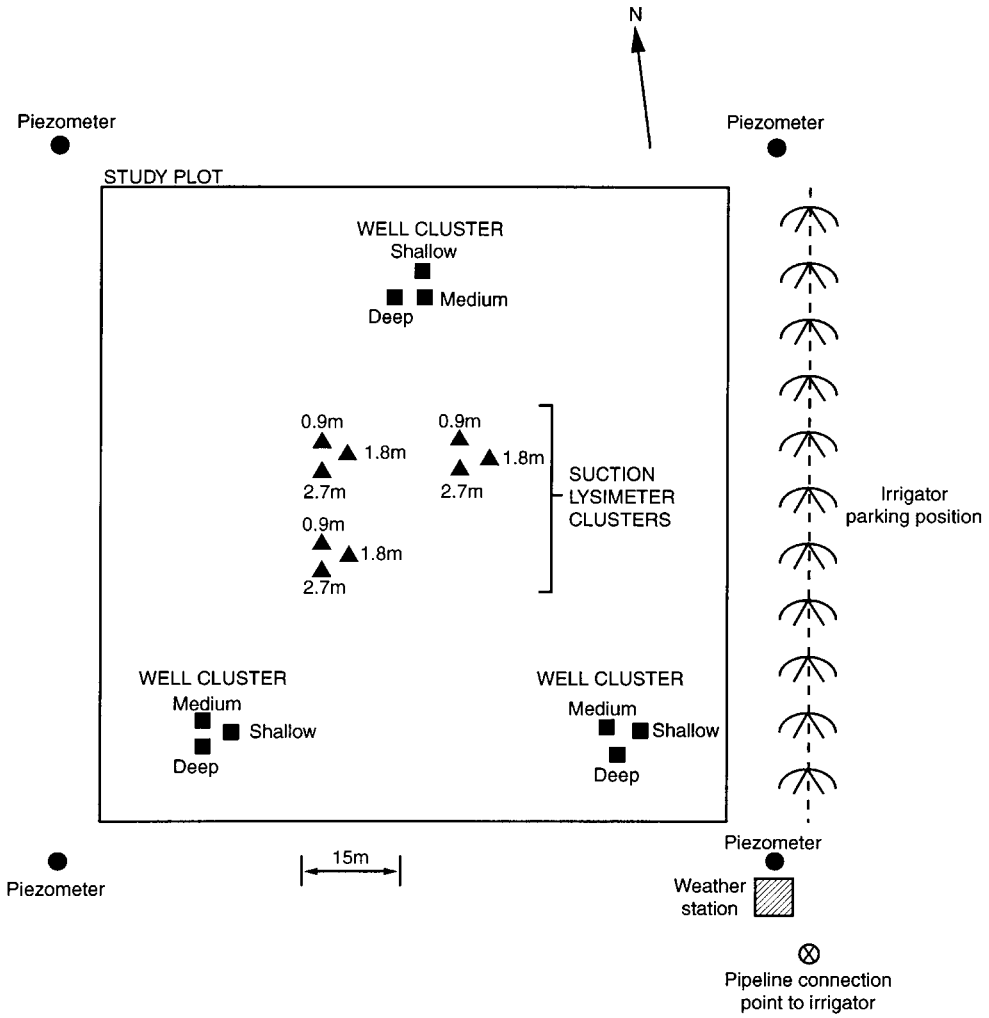


Fig. 5. Illustration of fomesafen PGW plot layout, Goldsboro, NC. Diagram shows piezometer clusters, lysimeter clusters, well clusters and irrigation equipment.

3.1.3 Agronomy during test period

Soybeans were planted on 1 June 1988 following spring 'discing' and fertiliser application. Fomesafen was applied to the emergent soybeans on 15 June 1988 (see Section 3.1.6), and the crop was grown to maturity. The primary soybean crop was harvested on 16 November 1988 and the plot 'disced' and immediately seeded with winter wheat.

3.1.4 Irrigation

A linear tracking irrigation system (Valley Industries, Nebraska, USA) was installed at the site to provide supplementary irrigation. The system was connected to a 15-cm irrigation well installed to a depth of 48·8 m, approximately 185 m west of the test plot. The well was screened from 24·4–35·1 m and 42·7–48·8 m and a pump permanently installed at 41·1 m.

3.1.5 Meteorology

Historical weather records were provided by the NOAA National Climatic Center, Ashville, North Carolina, USA, for the 'Goldsboro 1 SSW' weather station, located at the Seymour Johnson Air Force base (approximately 16 km from the test site). The 30-year (1951–1980) average precipitation at Goldsboro is 137 cm $year^{-1}$ and pan evaporation averages 152 cm $year^{-1}$. During the course of the PGW study, on-site weather conditions (wind speed, wind direction, rainfall, relative humidity, air temperature, soil temperature (5 cm and 20 cm), pan evaporation and solar radiation (pyranometer) were monitored every 30 s (mean readings every 60 min) with an automatic weather station (21X Micrologger, Campbell Scientific Inc., Logan, Utah, USA) positioned 9·1 m from the south-east corner of the study plot.

3.1.6 Fomesafen application

A single application of fomesafen was made to the site, 14 days after soybean planting, using a 228 g AI kg^{-1} formulation (Reflex™). The treatment was made using a tractor-mounted spray boom, at a rate of 560 g AI ha^{-1}. This equates to 133% of the maximum agricultural label rate (label 420 g ha^{-1}) for the product. At treatment, the soybeans were at the first trifoliate leaf

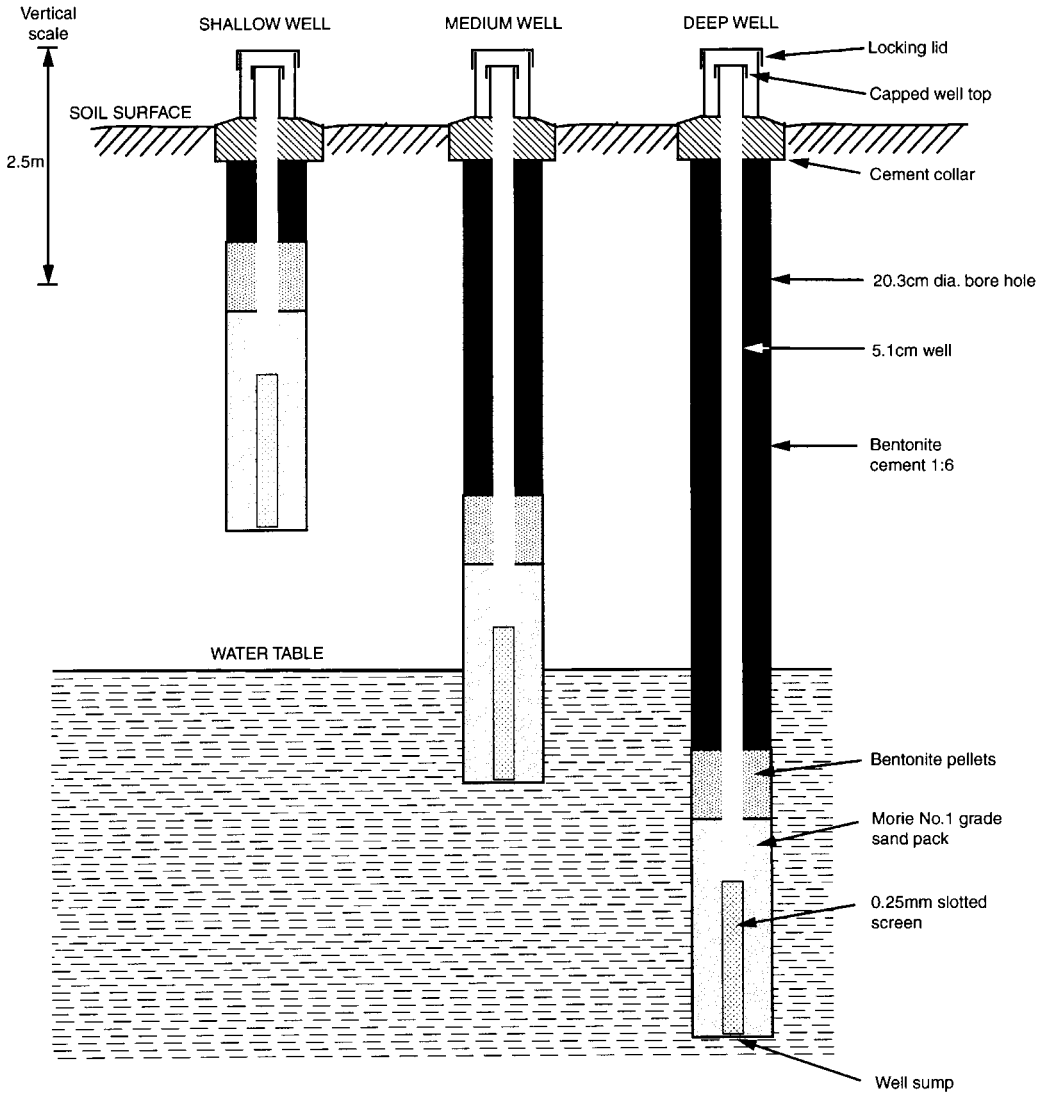


Fig. 6. Diagram of structure of wells (shallow, medium and deep) at fomesafen PGW site, Goldsboro, NC.

stage, and the crop canopy covered approximately 2·5% of the surface. The spray additive 'Ortho-77' (a non-ionic surfactant) was added to the spray tank to a final concentration of 2·5 ml litre^{-1}, as is also specified on the product label. Following application, irrigation was applied to supplement natural rainfall. In the first 12 months following application, the precipitation and irrigation total was 179·53 cm (143% of the 30-year average).

3.1.7 Field sampling procedures for residue analysis

3.1.7.1 Soil sampling. Samples of soil were collected one month before treatment (used as analytical control) and immediately post-application ('zero time'), 7 and 14 DAT, followed by 1, 2, 3, 4, 6, 9, 12, 15, 18 and 21 months after application. The plot was sub-divided into three sub-plots (A, B and C) using marker posts. Soil samples were taken along marked transects in each sub-plot with no transect used more than once throughout the study. Seven 'surface' cores were taken in each sub-plot, at each time interval. At zero time, two transects were used to collect two sets of seven 'surface' cores in each sub-plot, in order to examine the distribution of fomesafen over the entire plot. Three 'deep' soil cores were collected at each interval from the same transect as the 'surface' cores (but approximately 1 m behind the line of the 'surface' cores). 'Surface' soil was cored in two stages, 0–10 cm and 10–40 cm, using zero-contamination sampling techniques described previously (Section 2.1.5).

The 'deep' soil (40–224 cm) was cored using a tractor-driven ('Giddings') hydraulic ram corer. A progressive sampling procedure was used to produce cores of 40–102 cm and 102–164 cm, and similar procedures used to sample further, to 224 cm. A 30 × 60 × 40 cm deep pit was excavated by hand and a steel box 25 × 50 × 40 cm deep placed in the pit to prevent ingress of surface soil into the pit. A tractor with a hydraulic ram was then positioned with the press-rod over the pit. A 62-cm plastic corer tube (liner) was

placed inside a 124-cm steel zero-contamination corer of 5 cm diameter, with a 62-cm spacer above. A purpose-made steel sleeve was then fitted around the steel corer. The hydraulic press rod was used to push the corer and sleeve into the soil, within the 40-cm-deep pit, to a depth of 62 cm. The corer was then removed, leaving the sleeve in place, thereby preventing any collapse of soil from the core wall. The liner containing the 40- to 102-cm soil core was then removed from the steel cover. The zero contamination corer was again prepared as above, and pushed down within the sleeve left in the soil. The hydraulic ram was then used to force the core and sleeve down a further 62 cm to collect the 102- to 164-cm core. The corer was then removed, while the sleeve was retained in the ground. At the three-month sampling event, and at all subsequent samplings, soil samples were taken down to 224 cm. The depth of sampling was extended to ensure that no residues could be 'lost' between sampling events. These very deep samples were taken by inserting a 60-cm steel zero-contamination corer (2·5 cm diameter) through the 5-cm diameter sleeve, thereby preventing any collapse of soil from the core wall. The liner and core were then removed from the steel cover. All soil cores in their plastic liners were then capped and frozen, prior to shipment to the analytical facility for analysis for fomesafen residues.

3.1.7.2 Soil-pore water from suction lysimeters. To collect soil-pore water, suction lysimeters were sampled every two weeks by applying a vacuum (*c.*70 mbar) using a hand pump with vacuum gauge. Lysimeters yielded 50–100 ml soil-pore water with a vacuum of 15–25 millibars. To sample the pore water, the lysimeter discharge tube was placed in a Nalgene polyethylene bottle (250 ml) and the lysimeter gently pressurised to force all the soil-pore water into the sample bottle. The lysimeter was then re-evacuated to 70 millibars vacuum for a further two-week collection period. Samples were frozen in the field for shipment for subsequent analysis.

3.1.7.3 Ground-water from monitoring wells. Well water was collected one month before fomesafen application, from monitoring well clusters I–III, at zero time and at subsequent monthly intervals up to 33 months after application. Prior to sample collection, each well was pumped at 4 litre min^{-1} for 10 min over instrument probes, until pH, conductivity and temperature readings gave four consecutive values within certain limits ($\pm$0·01 pH units, $\pm$0·002 mho cm^{-1} conductivity and $\pm$0·2°C temperature), and visual observation showed the water to be clear. After purging, eight samples (*c.* 750 ml) were pumped into 1-litre Nalgene bottles (polyethylene) and stored frozen at −18°C within 4 h of sampling. Samples were maintained at −18°C during storage and transportation to Jealott's Hill Research Station, Bracknell, UK, using dry ice, until thawed for analysis. The eight samples taken from each individual monitoring well (approximately 6 litres) were pooled and five 1-litre portions taken for analysis. There was no pooling of water between monitoring wells.

3.1.8 Residue analysis

3.1.8.1 Soil. To minimise contamination of sub-surface cores by foreign soil particles from 'core-wall collapse', the top 1–2 cm of each core (except the 0–10 cm core) was discarded. The core sections were: 0–10, 12–25, 25–40, 42–56, 56–71, 71–102, 104–132, 132–162, 165–193 and 193–224 cm. Soil cores were sliced whilst frozen and still within the plastic liners, using an electric band saw. The soil was thawed and removed from the liners, and the replicate samples from identical depths and sub-plots combined (seven replicates for 'shallow' and three for 'deep'). Soils were sieved through a 2-mm mesh and thoroughly mixed after air-drying. Samples of homogenised soil (50 g) were fortified with an internal standard and extracted with methanol + 1 M hydrochloric acid (90 + 10 by volume; 80 ml) by refluxing for 2 h. The extracts were then filtered, prior to liquid–liquid partitioning into dichloromethane. The dichloromethane phase was evaporated to dryness and the residues taken up in deuterochloroform (0·6 ml) and if necessary methanol (50 µl) to dissolve any precipitate. The chloroform solution was analysed by [^{19}F]NMR using a JEOL GX400 instrument under the following conditions: [^{19}F]NMR 376 MHz; scan 15 015 Hz = 40 ppm; number of scans 12 000–24 000; repetition time 0·6 s; pulse width 3·5 s (90°C pulse = 7·8 µs); plot +5 to −5 ppm from the NMR reference marker. The limit of determination (LOD) was 0·01 mg kg^{-1} dry soil.

3.1.8.2 Soil-pore water. Suction lysimeter samples were pooled within each lysimeter depth, from the samples generated during each sampling month. Fomesafen from the soil-pore water was concentrated by adsorption onto 2·5 g of methanol-activated Lichroprep C-18 reverse phase silica (Merck, Germany), then eluted with methanol (25 ml followed by 100 ml). The methanol eluent was taken to dryness *in vacuo*, spiked with internal standard and solubilised with a small volume (*c.*1 ml) of dichloromethane. After again taking to dryness, the residues were dissolved in deuterochloroform (0·6 ml) and analysed by [^{19}F]NMR under the conditions described above. Ground-water samples were analysed using identical methodology. The LOD of fomesafen in soil-pore and ground-water was 1·0 µg $litre^{-1}$.

3.2 Results and discussion

A PGW study of the potential for fomesafen to move downward through the soil profile and into ground-water was carried out on a test plot exemplifying 'worst-case' conditions for leaching. The soils under-

lying the test area were typical of Inner Atlantic Coastal Plain soils of the south-eastern United States, being dominated by fine to coarse grade sands, with occasional deposits higher in clay content. The surface texture at the test site was characterised as a loamy sand of approximately 1% organic matter and typical of the Kenansville series. Kenansville loamy sands have moderate limitations of low fertility, leaching or droughtiness and, where cultivated, conservation practices are required. Measured vertical hydraulic conductivities generally ranged from 2·5 to 12 cm h^{-1}, reflecting the very coarse sandy texture in the soil profile and confirming the vulnerability of the site. During the course of the study, water-table depths remained shallow, varying from 5 to 6·1 m.

Residues of fomesafen in surface soil dissipated with a half-life of 7–8 weeks, falling from zero time levels of 0·26 mg kg^{-1} to 0·02 mg kg^{-1} at the end of the 21-month soil-sampling period (Fig. 7). Residues in soil fractions below 40 cm were generally $\leqslant$0·01 mg kg^{-1}. The very low levels of fomesafen detected on soil samples at depth was paralleled by the determination of only very small residues in soil-pore water collected from suction lysimeter units. A peak residue of 33 µg $litre^{-1}$ was determined at 1 m after three months, equivalent to a soil residue of approximately 0·008 mg kg^{-1} (below the 0·01 mg kg^{-1} limit of determination for soil). With irrigation and rainfall exceeding evapo-transpiration, this small mobile fraction continued to move through the profile and to dissipate. The maximum residue detected at 2 m was seen after seven months (12 µg $litre^{-1}$) and at 3 m after 10–12 months (5 µg $litre^{-1}$), with residues in all lysimeters returning to below limits of determination (<1 µg $litre^{-1}$) around 22 months after application.

No residues of fomesafen were detected in any ground-water samples taken up to 16 months after treatment. Trace levels of fomesafen ($\leqslant$1 µg $litre^{-1}$) were determined in the 'medium' depth well in Cluster I (the 'shallow' well was above the water table and therefore dry), between the 17- and 33-month sampling intervals. Similarly, small residues were also determined in the 'deep' well in Cluster I, at 17, 18, 20 and 33 months, and also in the 'medium' (18 and 20 months) and 'deep' (18 months) wells in Cluster II. No fomesafen residues were determined in any well located in Cluster III.

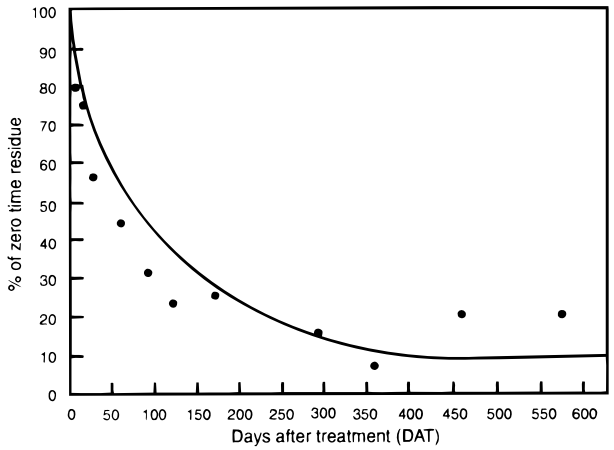


Fig. 7. The dissipation of fomesafen in surface soil during the PGW study, Goldsboro, NC.

The results of this study demonstrate that, under extreme conditions, fomesafen has the potential to move to shallow ground water, albeit at low concentrations. Although conducted on highly permeable soils, with shallow ground-water and extremely high precipitation, the movement of the test chemical in this study provides a rich source of data from which simulation models may be calibrated. These data will therefore be invaluable in extrapolating from this highly vulnerable setting to assess leaching potential in more typical and representative product use areas.

4 PREFERENTIAL MOBILITY STUDY USING TRACER DYES

4.1 Materials and methods

Following the fomesafen PGW study (Section 3), a small-scale tracer study was initiated to investigate potential preferential flow pathways in the soil surrounding the previously installed suction-cup lysimeters.

4.1.1 Plot preparation

An area of 1·52 × 4·57 m was selected over two suction-cup lysimeters, previously vertically installed at depths of approximately 2 and 3 m. Vegetation was removed by hand weeding and the soil surface smoothed to eliminate depressions or mounds that could prevent an even application of tracer and percolation water. Boundary boards were positioned along the edges of the test area to confine the tracer during application and to provide a stable base upon which the applicator boom could rest during application.

4.1.2 Test chemical and application

Pyranine (D & C No. 8) was employed as the tracer because of its low soil adsorption coefficient and its visible fluorescence when irradiated with UV light in light-coloured sandy soils. Approximately 400 g of pyranine were dissolved in 8 litres of water to provide a stock solution. Portions of this stock solution (400 ml) were added to a PVC reservoir containing water (20 litres). The solution was applied whilst moving back and forth along the guide boards that defined the test area; the boom comprised three equally spaced 110° flood-tip nozzles, mounted on an aluminium rod, pumped by a three-stage, 4·5-cm diameter submersible

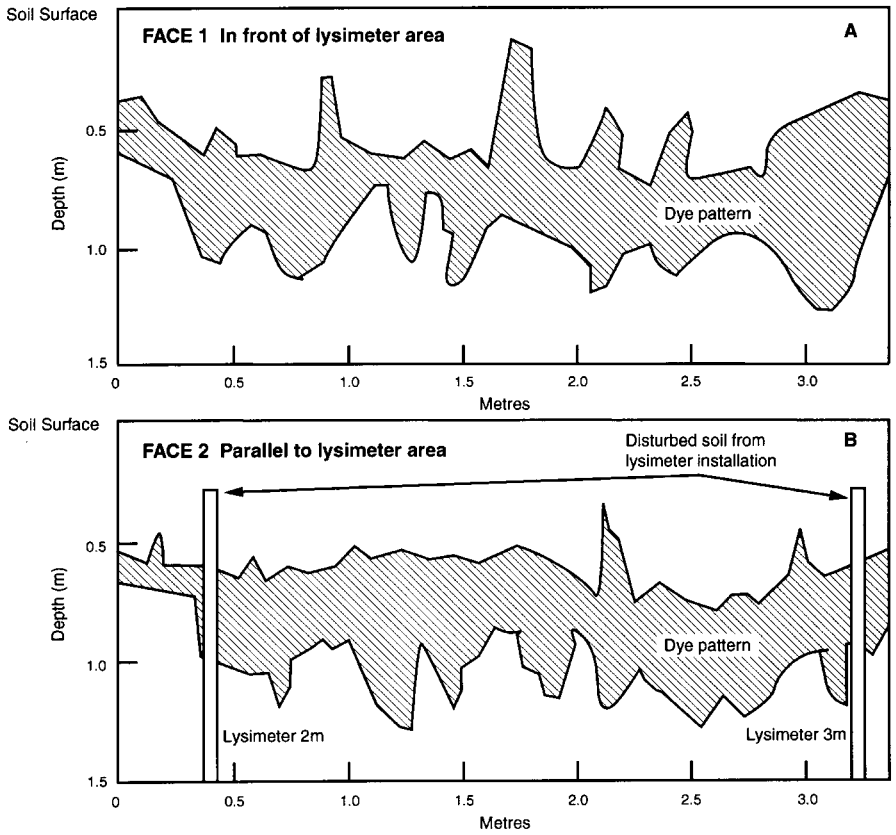


Fig. 8. Dye leaching profile through structured study soil at PGW fomesafen site. (A) dye pattern on exposed pit face in front of lysimeter installation area, and (B), dye profile around the exposed suction cup lysimeter installation area.

well pump (XP100-60, KV Associates, Falmouth, MA, USA). Approximately 2·4 litres of the stock solution were applied in this manner, in a total 120 litres of water. The remaining 5·6 litres of stock solution were diluted to 20 litres, and 10 litres of the resultant solution applied. The remaining 10 litres were then again diluted to 20 litres and the whole solution applied to the test area, resulting in a total pyranine application rate of 5·76 mg cm^{-2}. Following tracer application, the spray tank and application system were rinsed with water (230 litres), which was applied evenly to the soil surface. The total amount of water applied to the test plot during this was equivalent to *c.* 5·08 cm of rainfall over a 12-h period. The test plot was allowed to drain overnight and more water (750 litres) was applied evenly the following morning using the same technique. The plot was then allowed to drain again, prior to excavation.

4.1.3 Excavations & UV irradiation

A profile across the area to which the tracer had been applied was exposed mechanically using a tractor-mounted back-hoe (JCB). Initial excavations exposed a pit area of approximately 5 m in length (parallel to the suction-cup lysimeters and application area), 7 m in width and 2 m in depth. The pit area was then manicured by hand, using shovels and trowels, in an effort to square the pit 'face' and to ensure a parallel alignment with the unexposed suction lysimeters. Knives were used to pick the soil at the pit 'face' to remove any contaminated 'in-fill' and to delineate the soil structure. The plot area was then covered with thick black polyvinyl chloride (PVC) sheeting to exclude natural light and UV lights positioned within the darkened pit to provide visible fluorescence of the pyranine tracer at the pit 'face'. Visual and photographic assessments of the leaching pattern of the fluorescent tracer in the native soil profile were recorded.

Further manual excavations were completed by carefully shaving back the 'face' of the pit, using shovels, to expose the 2- and 3-m suction-cup lysimeters. The plot area was again covered and the soil irradiated with UV lights. Visual and photographic assessments of the leaching pattern of the fluorescent tracer in and around the installation channels of the suction lysimeters were recorded and compared to those of the previously recorded surrounding soil profile.

4.2 Results and discussion

Tracer experiments can provide useful evidence of flow patterns, movement mechanisms and ground-water recharge, in field leaching studies. In this experiment, a pyranine tracer was use to evaluate the flow patterns in a structured sandy soil and to test the integrity of pre-

viously installed suction-cup lysimeters. In this test, similar leaching profiles were observed for both the native surrounding soil profile and the exposed suction-cup lysimeter installations, indicating no preferential flow along lysimeter installation channels (Fig. 8). In both cases, the advancing wetting front, containing the pyranine tracer, appeared fairly uniform across the upper boundary of flow, with distinct regions or 'fingering' of tracer extending to 1·25 m below ground surface, at the lower boundary. Finger widths varied from 15 to 60 cm at the upper boundary, to 2·5 to 20 cm at the lower boundary. With the exception of the random 'fingering', no specific preferential flow paths were noted in the soil horizon.

5 MATHEMATICAL MODELLING

5.1 Soil, crop, hydrologic and application input parameters

Soil, crop, hydrologic and fomesafen application input data, generated during the fomesafen PGW study (Section 3) were entered into the PRZM model *via* a single input file.[10] Weather data, including those recorded by the on-site weather station at the PGW site, were input as a separate file (see Section 5.2). The soil profile being simulated was described by soil characterisation results obtained from a series of borings at the fomesafen study site. Erosion and run-off simulation was prevented by setting the crop run-off curve numbers to low values so that this loss route was minimised. Actual sowing, emergence and maturity dates for both the primary soybean crop (to which the fomesafen was applied) and the following wheat crop were used as model input parameters, together with soil half-life estimates of 100 days for surface soils (0–28 cm), and 200 days for sub-soils (below 28 cm). During the early modelling process, it was noted that fomesafen adsorption in the top layer of surface soils (0–5 cm) was being considerably underestimated and the input value for surface adsorption was subsequently increased to 10 times the measured laboratory value. Measured adsorption values in soil layers below 5 cm were used directly as model inputs. Initial modelling assessments gave poor agreement between observed (Section 3) and simulated results and required calibration of the model through the adjustment of the dispersion coefficients. Dispersion inputs were varied linearly with depth from 0 and 100 $cm^2\ day^{-1}$

5.2 Weather data input files

The primary weather input file used for these simulations was developed from data recorded from the on-site weather station at the PGW site. The input file included daily values for precipitation, average air temperature and pan evaporation. Where specific on-site values were missing due to instrument malfunction, the data were supplemented by values available from the local National Oceanic and Atmospheric Administration (NOAA) monitoring location, at the Seymour Johnson Air Force Base, in Goldsboro, NC, located approximately 8 km north-west of the PGW site. Separate weather input files were developed for longer-term simulations.

The Raleigh/Durham NOAA monitoring station (W13722) is located approximately 100 km north-west of the PGW site being simulated and provided long-term (36-year) historical weather data from which to construct PRZM input files to estimate the impact of annual fomesafen applications to the PGW site over a 36-year period. The Raleigh/Durham area averages 106·8 cm of rainfall in a year, slightly drier than the study site location (Seymour Johnson Air Force Base averages 124·4 cm annually). The Wilmington NOAA monitoring station (W13748) is located approximately 120 km south of the PGW site, in a coastal position. The Wilmington area averages 136·4 cm of rainfall in a year, slightly wetter than the PGW study site location. Using these input values, a two-year fomesafen PGW study was simulated and the results compared to those generated by chemical assay. Subsequently, a long-term simulation of 36 years of continuous soybean/fomesafen use was run for two locations of differing annual rainfall, and the resultant ground-water concentrations estimated.

5.3 Results and discussion

In the fomesafen prospective ground-water study (PGW), individual measurements were made for soil-pore water concentrations at approximately 1, 2 and 3 m below ground surface (composites of the three lysimeters at each depth), whilst three separate measurements were made for soil and ground-water residues, at each sampling interval. For comparison to model outputs, when all three soil or ground-water measurements were below the limit of determination (0·01 mg kg^{-1} or 1·0 µg $litre^{-1}$, respectively), then this was presented as a 'zero residue'. When positive residues were determined in soil or ground-water samples, the mean residue was calculated, taking the 'non-detects' to be one-half of the respective LODs.

5.3.1 Two-year fomesafen PGW simulation

5.3.1.1 Soil residues. PRZM predicted soil residues for the 0- to 10-cm, 10- to 25-cm and 25- to 40-cm horizons, following a spring application to soybeans. These were compared with results obtained from the associated fomesafen PGW study (Figs 9(a), (b) and (c)). Measured fomesafen soil residues in the 0- to 10-cm and 10-

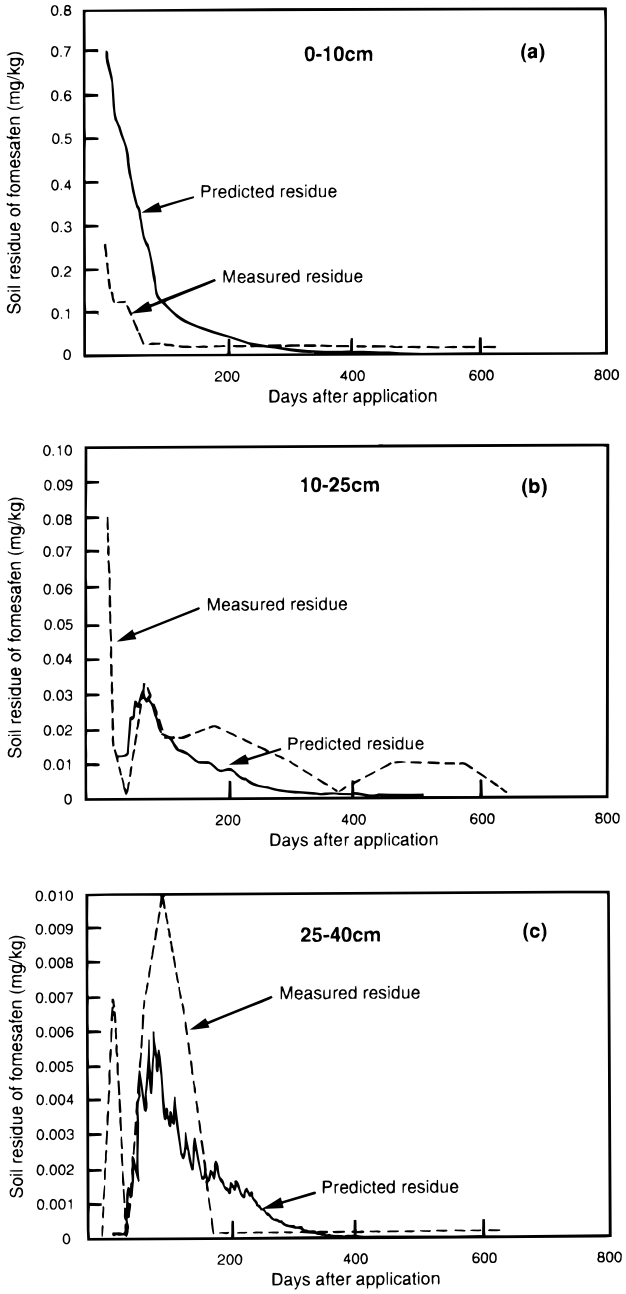


Fig. 9. PRZM-predicted residues of fomesafen compared to measured soil residues obtained from (a), 0–10 cm, (b), 10–25 cm and (c), 25–40 cm horizons.

to 25-cm layers were in reasonable agreement with the modelled values in the first 100 days following application. Thereafter, modelled results tended to underestimate soil residues, perhaps due to fomesafen adsorption increasing with time. However, for the purposes of this study (simulating soil-pore and ground-water concentrations) the agreement between modelled and measured soil residues was adequate.

5.3.1.2 Soil-pore water residues. In the fomesafen PGW study, soil-pore water was sampled using suction lysimeters at depths of approximately 1, 2 and 3 m. The leachate entering these units was collected over a period of 20–40 days of continuous vacuum, with samples from each depth pooled, at each sampling interval, to provide sufficient sample volume for the required LOD (1 μg litre^{-1}). Chemical assays therefore provide an average value of fomesafen concentration for the period of collection. PRZM was used to simulate the time profile of fomesafen concentrations at various depths, as a series of breakthrough curves. Values of the dispersion coefficient varying linearly (with depth) between 0 and 100 cm^2 day^{-1} resulted in good agreement between the observed chemical assay results and model predictions (Figs 10(a) and (b)).

5.3.1.3 Ground-water residues. PRZM predicted no detections in ground water during the first year of the study, a result that correlated precisely with the results of chemical assays (Fig. 11). Detections were predicted to occur at 16–18 months after application and reach a plateau of approximately 1 μg litre^{-1}. Again these results were in agreement with the chemical assays.

5.3.2 Thirty-six-year continuous soybean fomesafen use simulation

Figure 12 shows the results of long-term simulations with the calibrated PRZM model and displays a time

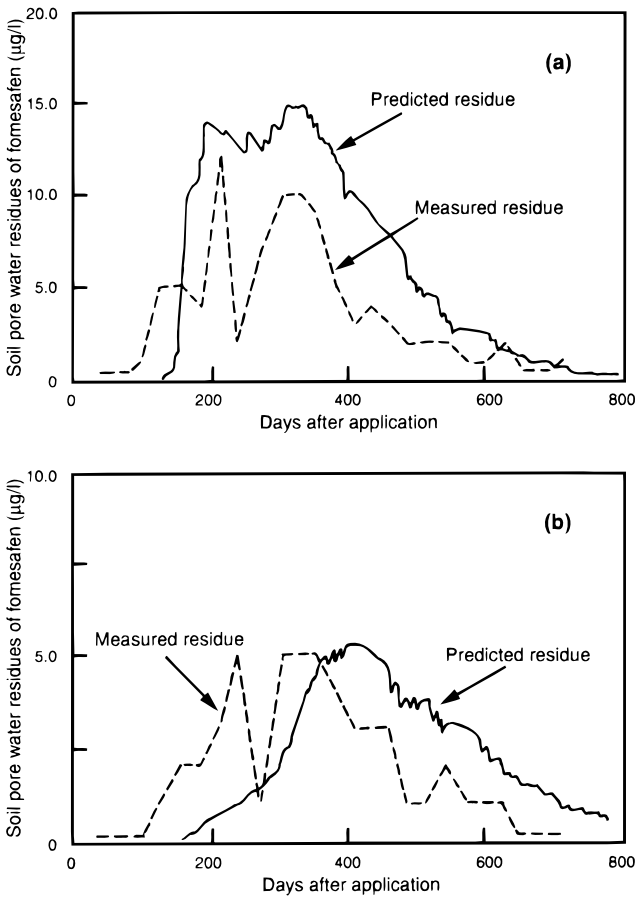


Fig. 10. PRZM-predicted versus measured soil-pore water residues of fomesafen. Suction lysimeters (a) at 1·8 m and (b) at 2·7 m.

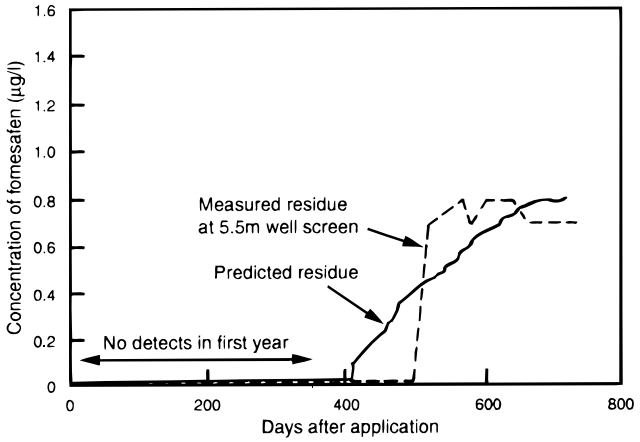


Fig. 11. Predicted and observed concentrations of fomesafen in ground-water.

series of the estimated fomesafen concentration at a 5 m depth with two sets of weather conditions, assuming that soybeans were grown continuously on a 'worst-case' sandy soil, with fomesafen applications each spring, for 36 years. Although unrealistic in terms of agronomic practices, the simulation does serve to provide an insight into the potential for build-up of residues in ground-water over time. The results show that the expected concentrations vary according to water flux, from year to year. At Raleigh/Durham, NC, ground-water residues are predicted to average around 0·15 µg litre^{-1}, with peaks to 0·4 µg litre^{-1}. At the wetter Wilmington NC location, ground-water residues are estimated to range from 0·3 to 1·3 µg litre^{-1}, with an average concentration of around 0·7 µg litre^{-1}. The modelling work usefully extended the data on ground-water residues over two years to provide an insight into potential fomesafen ground-water concentrations, following many years of repeat applications. No build-up of residues was predicted.

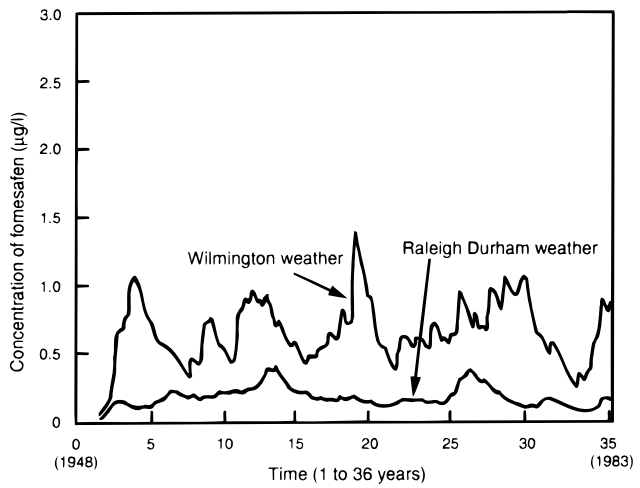


Fig. 12. Predicted concentration of fomesafen in soil-pore water at 5-m depth using weather data from Wilmington for 1948 and 1983, and from Raleigh/Durham for 1948 to 1983.

6 GROUND-WATER MONITORING OF POST-EMERGENCE HERBICIDES

6.1 Materials and methods

6.1.1 Selection of ground-water sampling sites (wells) and study timelines

A 95-well ground-water monitoring programme was conducted in Germany in 1985. Public and private wells in seven Federal states were selected in areas with soils vulnerable to leaching and which had received many fluazifop-butyl applications. Ground-water was monitored for fluazifop, the major acid metabolite of the herbicide fluazifop-butyl (Fusilade). In 1989, fluazifop-P-butyl replaced fluazifop-butyl as the active ingredient in Fusilade. In 1990 a further 39 wells (some of which had been used in the 1985 study) were selected in Lower Saxony State (Niedersachsen) to monitor for fluazifop and the 5-(trifluoromethyl)-2(1*H*)-pyridinone metabolite. Additionally, fluazifop and fomesafen were monitored in 12 wells in the Friuli region of northern Italy during 1989–1990. Eleven of the original 12 wells were sampled again in 1992 and 1994 for fluazifop only. Well locations in all monitoring studies were chosen in areas adjacent to agricultural land used for arable farming, and receiving high rates of fluazifop-butyl and/or fomesafen in vulnerable soils with a shallow water table, in order to assess the potential for ground-water contamination under these 'worst case' conditions. In the Friuli region of Italy, ground-water reaches the surface where two geologically different regions meet at a 'spring line'. Ground-water samples were taken from both sides of this 'spring line'. Tables 1A and B provide additional detail.

6.1.2 Field sampling procedures

In the fluazifop monitoring programme in Germany, between five and seven samples were collected from each well over a period of 18 months (July 1985 to December 1986). In the subsequent fluazifop and 5-(trifluoromethyl)-2(1*H*)-pyridinone monitoring programme in Germany in 1990 samples were taken one, two and five months after application of fluazifop-butyl in May. All wells in both studies were pumped prior to sampling to remove standing water from the borehole. Samples were collected either from taps attached to the wells or from the open field shallow wells by a hand-held pump into 2·5-litre amber glass sample containers with PTFE screw fitting lids. Bottles and tops were flushed with several litres of well water prior to sample collection. Sample containers were filled and stored at 5°C prior to shipment and analysis.

In the Friuli region study in 1989–1990, wells were sampled five times at approximately three-monthly intervals between November 1989 and November 1990 (for fluazifop and fomesafen analysis). Eleven of the same 12 wells were sampled (4 and 5 November 1992,

TABLE 1A
Location, Well Depth and Agronomic Details for a Selection of Sampled Wells (95-Well Monitoring Study in Germany, 1985–1986)

Well information	*Number of wells*						
	Baden-Württemberg	*Bayern*	*Hessen*	*Niedersachsen*	*Nordrhein-Westfalen*	*Rheinland-Pfalz*	*Schleswig-Holstein*
Depth of well:							
Shallow (0–20 m)	5	5	1	8	8	2	1
Medium (20–50 m)	7	2	0	18	5	0	7
Deep (>50 m)	1	2	2	11	2	1	5
Karst spring	2	0	0	0	0	0	0
Land utilisation							
>70% arable farming	13	5	2	24	11	3	4
Mixed (arable forest/ small-holding)	2	3	1	11	2	0	4
Fallow/grazing and forest	0	1	0	2	1	0	5
Vines	0	0	0	0	0	0	0
No information	0	0	0	0	1	0	0

and 16 and 17 November 1994) for fluazifop analysis only. A maximum of 900 ml water was sampled into a 1-litre wide-mouth brown polyethylene storage bottle (Nalgene), and between four and 10 bottles collected at each sampling event. Samples were then frozen within 25 h of sampling and shipped for analysis.

6.1.3 Sample analysis

Various analytical procedures were employed during the monitoring programmes conducted between 1985 and 1994. The methods used for each monitoring study are described.

TABLE 1B
Location, Well Depth and Agronomic Details for a Selection of Sampled Wells (39-Well Monitoring Study in Niedersachsen, 1990, and 12-Well Monitoring Study, Northern Italy, 1990, 1992 and 1994)

Well information	*Niedersachsen*	*Northern Italy*	
No. of wells	39	12	
		Above spring line	Below spring line
Location	—	4	8
Land utilization: % Arable			
<40%	1	0	0
40–60%	10	0	0
60–100%	28	4	8
Well depth (m)			
<20	12	1	3
20–30	9	1	1
30–60	13	2	2
60–90	5	0	0
>90	0	0	2

6.1.3.1 Fluazifop and fomesafen: Method (A): (Italy monitoring samples, 1990). Water (500 ml) was extracted by passing through a preconditioned (10 ml methanol) 47-mm Empore C_{18} extraction disc (Analytichem International, now Varian Sample Preparation Products) at a flow rate of approximately 100 ml min^{-1}. The disc was allowed to dry and was then eluted under vacuum with methanol (10 ml). The eluate was evaporated to dryness, re-dissolved in methanol +0·4% acetic acid solution (55 + 45 by volume; 1 ml) prior to HPLC analysis (HPLC conditions 1).

6.1.3.2 Fluazifop only: Method (B): (Germany monitoring samples, 1990; Italy monitoring samples, 1992, 1994). Water (500 ml) was acidified to pH 1 with concentrated hydrochloric acid, methanol (to give 10 ml $litre^{-1}$) was added and the sample extracted on a prepared Sep-Pak C_{18} (1 g) Environmental Cartridge. After application, the cartridge was washed with deionised water (5 ml), air-dried and further washed with hexane (2·5 ml). The analyte was eluted sequentially with acetonitrile (6 ml) and methanol (6 ml). The combined fractions were reduced to dryness *in vacuo* and redissolved in acetone (1 ml) prior to derivatisation and analysis by GC/MS. Method (C): (Germany monitoring samples, 1985). Water (500 ml) was acidified to pH 1 with concentrated hydrochloric acid, prior to solid-phase extraction on a pre-conditioned (2 ml methanol; 1 ml 0·1 M HCl) C_2-Bond Elut cartridge (500 mg) (flow rate 3 ml min^{-1}). After application the cartridge was eluted with acetonitrile + water (70 + 30 by volume; 1·5 ml) and 0·1 M hydrochloric acid added to the eluate to produce an aqueous acetonitrile (1 + 1 by volume) solution. The eluate was then loaded onto a pre-conditioned (as above) C_{18} Bond-Elut column. The column was washed with acetonitrile + water (70 + 30 by volume;

300 µl), dried by passing air through the cartridge for 1 min, then eluted with acetonitrile + water (80 + 20 by volume; 900 µl) prior to analysis by HPLC (HPLC conditions 2).

HPLC conditions (1): Column and packing: Spherisorb S50DS2, 12·5 cm × 4·6 mm ID; mobile phase: methanol + aqueous acetic acid (4 ml litre^{-1}) (55 + 45 by volume); flow rate 1·5 ml min^{-1}; UV detection wavelength: 270 nm. HPLC conditions (2): column and packing: 25 cm × 4·6 mm Altex 5 µm ODS with C_{18} Adsorbosphere guard column; mobile phase: acetonitrile + water + methanol + phosphoric acid (225 + 285 + 30 + 1, by volume) flow rate: 2·0 ml min^{-1}; UV detection wavelength: 270 nm. GC/MS Conditions: Derivatives were analysed by GC/MS in single ion monitoring mode (SIM) using a Hewlett Packard 5890 series GC interfaced to an HP 5970B mass selective detector. Column: J&W DB17 (cross-linked dimethyl phenyl polysiloxane) fused silica wall coated open tubular capillary column. 10 m × 0·187 mm ID. Film thickness 0·3 µm. Injector: splitless, 1·8 min purge delay. Oven temperature: 45°C (2 min), then 20°C min^{-1} to 280°C (hold 1·25 min). Mass spectral conditions: Ionisation: electron impact; Multiplier: 3000 V; Dwell time: 150 ms. The limit of determination for all fluazifop methods was 0·1 µg litre^{-1}, and for fomesafen it was 0·1 µg litre^{-1} except for July 1990 only (0·2 µg litre^{-1}).

6.1.3.3 Fluazifop and 5-(trifluoromethyl)-2(1H)-pyridinone analysis. The metabolites were extracted simultaneously using extraction Method B, above. Fluazifop was methylated using diazomethane and quantified as the fluazifop-methyl ester. 5-(Trifluoromethyl)-2(1*H*)-pyridinone was derivatised to the corresponding *tert*-butyl-dimethylsilylether derivative with *N*-methyl-*N*-(*tert*-butyl-dimethylsilyl)trifluoroacetamide + 1% *tert*-butyl-dimethylchlorosilane. Derivatives were analysed by GC/MS using the conditions described above.

6.2 Results and discussion

The objective of the ground-water monitoring programmes conducted in Germany and Italy was to analyse ground-water from a number of public and private wells located adjacent to agricultural land and assess any potential risk of contamination from fluazifop, the primary acid metabolite of fluazifop-butyl and fluazifop-P-butyl. In the 1990 German study, 5-(trifluoromethyl)-2(1*H*)-pyridinone, a minor metabolite of fluazifop-butyl and fluazifop-P-butyl was also monitored. The structures of parent compounds and metabolites are illustrated in Fig. 13. The wells chosen for the German monitoring programmes were selected in areas of high product use, and in vulnerable ground-water areas (i.e. shallow water table or permeable soil/geology).

The Friuli region of northern Italy is also a vulnerable ground-water region and has been extensively monitored.[12] The local geology consists of two distinct areas; a high plain formed substantially from stony soils with an arable stratum low in organic matter, lacking in clays, and thus highly permeable, and a low plain formed exclusively from mud-clay soils with quite opposite characteristics. Ground-water reaches the surface where the two regions meet, at a 'spring line'. Studies on the hydrogeology of the region conclude that it is possible for the waters of the high and low plain regions to come into contact. Thus, it is possible that chemical contamination introduced into the environment of the high plain could contaminate both the high-plain strata and artesian wells in the low-plain region.

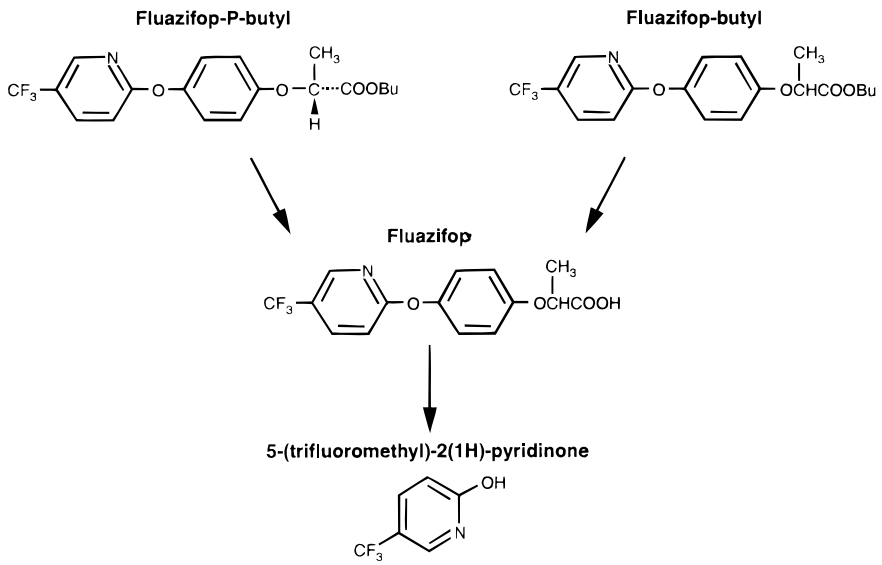


Fig. 13. Molecular structures of fluazifop-butyl and fluazifop-P-butyl and their metabolites.

Ground-water samples were taken from both sides of the 'spring line' and monitored for residues of fluazifop (from recent Fusilade applications) and fomesafen (from recent Flex applications (Table 1A and B).

The 1985 German ground-water survey showed that, of the 95 raw water wells sampled at regular intervals over a period of 18 months (605 samples), none contained measurable residues of fluazifop (LOD 0·1 μg litre^{-1}). Similarly, no residues of fluazifop were determined in any of the water samples collected one, two and five months after commercial application of Fusilade (LOD 0·1 μg litre^{-1}) from 39 wells in Niedersachsen where the use of the herbicide is considered to represent the 'worst case' in terms of application rate, timing and soil type.

In the Friuli region of Northern Italy no detectable residues (LOD 0·1 μg litre^{-1}) of the metabolite fluazifop were found in any of the water samples collected from 12 wells in 1990, 1992 or 1994. Similarly, no detectable residues of fomesafen were found in any of the samples (LOD (1990) 0·2 μg litre^{-1} and subsequently 0·1 μg litre^{-1}).

The results of these monitoring programmes indicate that the commercial use of Fusilade (fluazifop-P-butyl or fluazifop-butyl) and Flex (fomesafen) over a number of years poses negligible risk of ground-water contamination, even in regions of permeable soil and a shallow ground-water table.

7 CONCLUSIONS

This paper demonstrates the need for a flexible approach to environmental fate studies to develop an environmental profile of a compound's mobility and degradation in surface soil and sub-soil environments. This knowledge is essential for environmentally responsible stewardship of a product in commercial use.

The use of radiochemical techniques in both laboratory and field studies is often necessary to track a compound through its many stages of transformation and transport. These results, together with those from larger-scale monitoring studies help to complete the environmental profiles of individual products. They also serve as a validation of conventional laboratory studies (e.g. aerobic soil metabolism, column leaching studies) and aid in the design and development of new laboratory-based environmental fate studies (e.g. laboratory-based sub-soil degradation studies).

The examples provided in this paper illustrate the use of a variety of small and large-scale field studies to address specific environmental fate questions for particular products. The data generated in these diverse field studies are invaluable for refining and validating mathematical models for subsequent use in simulating environmental concentrations under a variety of potential product-use situations.

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